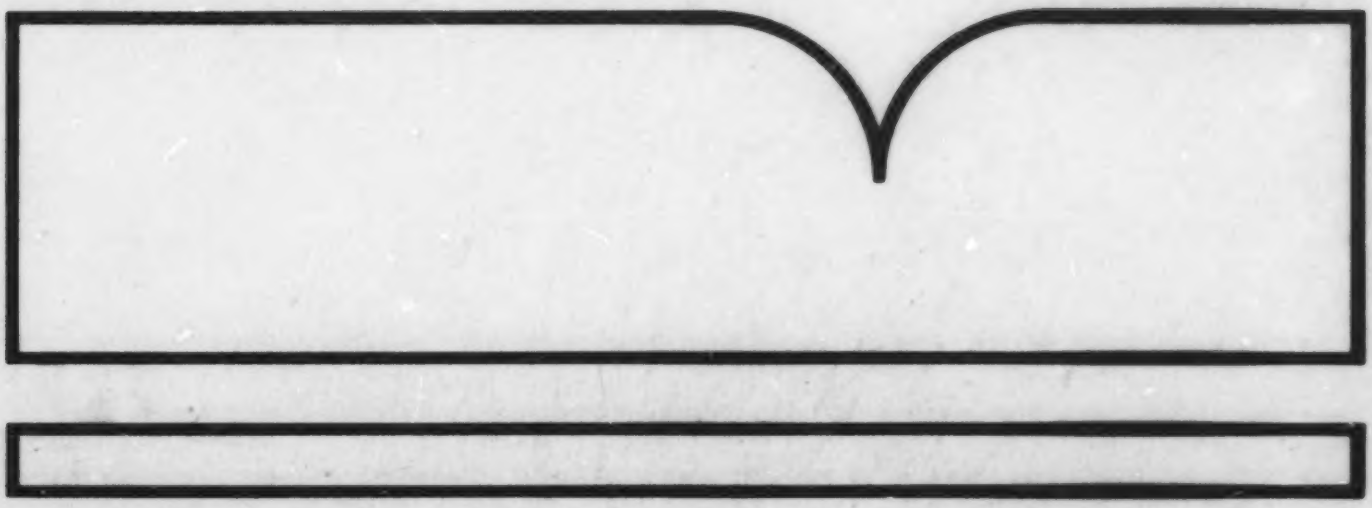
PB81-233413

Effects of Equilibration Time on Photoreactivity of the Pollutant DDE Sorbed on Natural Sediments

(U.S.) Environmental Research Lab.
Athens, GA

Jul 81



U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RE PB81-233413
EPA-600/J-81-201	Journal Article	

4. TITLE AND SUBTITLE	5. REPORT DATE
Effects of Equilibration Time on Photoreactivity of the Pollutant DDE Sorbed on Natural Sediments	July 1981
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Richard G. Zepp and Patricia F. Schlotzhauer	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory U.S. Environmental Protection Agency College Station Road Athens GA 30613	AARB1A, ACBE1A
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S. Environmental Protection Agency--Athens GA Environmental Research Laboratory College Station Road Athens GA 30613	Journal Article
	14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES
Published in: Chemosphere. 10(5):453-460, 1981.
Contact: R.G. Zepp, FTS 250-3428

16. ABSTRACT

Photolysis of the hydrophobic pollutant 1,1-bis(p-chlorophenyl)-2,2-dichloroethylene (DDE) was studied in aquesous suspensions of three well-characterized sediments. Results of the study can be described by equations that are based on a kinetic model that takes into account sorption kinetics. Analysis of the kinetic data using this model indicates that the sorbed DDE is, at equilibrium, about half in reactive sites and half in sites where the DDE is unreactive.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

PRODUCT OF:
NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	8
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

Chemosphere, Vol. 10, No. 5, pp 453 - 460, 1981
Printed in Great Britain

EPA-600/J-81-201
Journal Article

EFFECTS OF EQUILIBRATION TIME ON PHOTOREACTIVITY OF THE POLLUTANT DDE SORBED ON NATURAL SEDIMENTS

Richard G. Zepp and Patricia F. Schlotzhauer

Environmental Research Laboratory
U.S. Environmental Protection Agency
Athens, GA 30613

ABSTRACT — Photolysis of the hydrophobic pollutant 1,1-bis(p-chlorophenyl)-2,2-dichloroethylene (DDE) was studied in aqueous suspensions of three well-characterized sediments. Results of the study can be described by equations that are based on a kinetic model that takes into account sorption kinetics. Analysis of the kinetic data using this model indicates that the sorbed DDE is, at equilibrium, about half in reactive sites and half in sites where the DDE is unreactive.

INTRODUCTION

Recent studies of the photoreaction of pollutants in aqueous suspensions of natural sediments (1-3) have been conducted by equilibrating pollutants in suspensions for short periods (usually less than 2 days) prior to irradiation. These conditions differ from those that often occur in the environment where pollutants may remain sorbed in soil or bottom sediments for long periods before being introduced into the water column of a water body by runoff or resuspension.

Procedures used in the prior studies were based on the assumption that sorption of pollutants to natural sediments is a rapidly reversible process. Karickhoff (4), however, has demonstrated that at least part of the pollutant that sorbs to sediments does not readily exchange with the bulk water. The size of this slowly exchangeable part increases with time, reaching equilibrium over a period of days or weeks. The slowly exchangeable part also is not extractable by brief shaking with hexane. These findings suggest that the earlier studies of photolysis of sorbed pollutants may have overlooked an important aspect of the problem: the effects of sorption kinetics on photoreactivity.

The present study explores these effects using well-characterized natural sediments and the pollutant 1 1-bis(p-chlorophenyl)-2,2-dichloroethylene (DDE). DDE was selected for the study because it is stable in soils and sediments over long periods of time, it has a high tendency to partition to sediments, its photochemistry has been previously studied (2,5), and it can be analyzed at very low concentrations. The main objective was to determine the effects of equilibration time on the photolysis rate of the sorbed DDE. As used in this paper, the term "equilibration time" specifically refers to the period between the introduction of the pollutant to the suspension and the beginning of the irradiation period. Also reported are procedures for the efficient extraction of pollutants from sediments and for the introduction of pollutants into sediment suspensions.

EXPERIMENTAL

Materials. The DDE, obtained from Aldrich Chemical Co., was purified by recrystallization from 95% ethyl alcohol. Sediment samples were taken from a set obtained and characterized as described elsewhere (6). Properties of the sediments used in the present study are summarized in Table 1. γ-Methoxy-m-trifluoromethylbutyrophenone (MTB) was synthesized and purified as described elsewhere (2,3). Solvents were purchased from Burdick and Jackson.

Table 1. Properties of sediments used in study.

Sample	Source	pH 1:1	CEC /100g	Total N%	Org. C%
EPA 12	Soil Sample, Manchester, OH	7.63	13.53	0.214	2.33
EPA 13	Sediment, Ohio River, Ceredo, WV	6.90	11.86	0.167	3.04
EPA 26	Sediment, Mississippi R., McLure, IL	7.75	20.86	0.152	1.48

Preparation of Suspensions. Reproducible analyses for DDE could not be accomplished using the whole sediments, presumably because it was not possible to obtain reproducible aliquots of the suspensions even after vigorous stirring. Accordingly, the suspensions were fractionated as previously described (2) and the finely divided, clay-sized particles were used in the studies. Sediment concentrations were adjusted to range from 80 to 100 milligrams per liter.

The DDE was introduced to the sediment suspensions through sublimination (7). A thin layer of solid DDE (1 mg) was coated on the inside of a glass cup that was suspended over the magnetically stirred sediment suspension (1.5 liters) in a closed container. After stirring for 15 hours, the concentration of DDE in the suspension typically reached 5 to 10 micrograms per liter. The cup was removed and the DDE-suspension mixture was allowed to equilibrate with stirring. The suspensions containing MTB (5.0×10^{-7} M) were prepared as previously described (3). To establish the fraction of a chemical that was sorbed, portions of the suspensions were centrifuged and the supernatant and sediment were analyzed. With DDE, 90 to 98% was sorbed in each suspension at time zero and with MTB, over 95% was dissolved in the aqueous phase.

Analysis. A variety of procedures were tried to rapidly and quantitatively recover DDE from the sediment suspensions. Nearly quantitative (over 90%) recovery of the DDE was achieved by first adding acetonitrile to the suspensions (25% by volume) then adding an equal volume of isooctane that contained an internal standard. The resulting mixture was agitated for 1 minute on a Vortex-Genie shaker then placed in a sonicator for one hour. The organic layer was analyzed by gas-liquid chromatography employing a Tracor MT-222 gas chromatograph equipped with a ^{63}Ni electron capture detector and a 2 m in length by 2 mm i.d. column containing 3% SE-30 on 80/100 Gas Chrom Q. The precision of the analysis, expressed as standard deviation over mean, was typically $\pm 5\%$. For comparison, in some of the studies the DDE was extracted using the same procedure but without adding the acetonitrile to the aqueous phase.

Photolysis Procedures. With the exception of the experiments with EPA-13 sediments, irradiations were performed in a specially constructed 2-liter flask equipped with flat windows. Studies of EPA-13 suspensions were conducted using a similar flask that was one liter in volume. The light source was a 450-watt, medium-pressure mercury lamp. The light was filtered through 4 mm of borosilicate (pyrex) glass to block wavelengths shorter than 300 nm. The sediment suspensions or solutions (1450 ml) were vigorously stirred throughout the irradiation period and aliquots were periodically removed with a 3-ml pipet that had a truncated tip. The light intensity was monitored by periodically exposing ferrioxalate actinometers (8) through a window in the side of the lamp housing. Controls established that the concentration of DDE and MTB in the sediment suspensions did not decrease in the dark over the usual time scale of a kinetic run and that less than 5% of the DDE or MTB was sorbed to the stirring bar and the walls of the reaction vessel.

RESULTS

Studies of the photolysis of DDE in suspensions of three different sediments indicate that the length of equilibration time influences the photolysis kinetics. Typical data are shown in Figures 1 through 3. Each kinetic point represents the mean concentration of DDE determined in three aliquots of suspension. In each figure, C_o and C are used to symbolize the initial concentration and the concentration after irradiation, respectively. Concentrations of DDE used in Figures 1 through 3 were determined by first adding acetonitrile to the aliquots as discussed in the Experimental Section, next extracting the DDE by thorough agitation with isooctane, and finally analyzing the isooctane for DDE. At time zero, the DDE was more than 90%

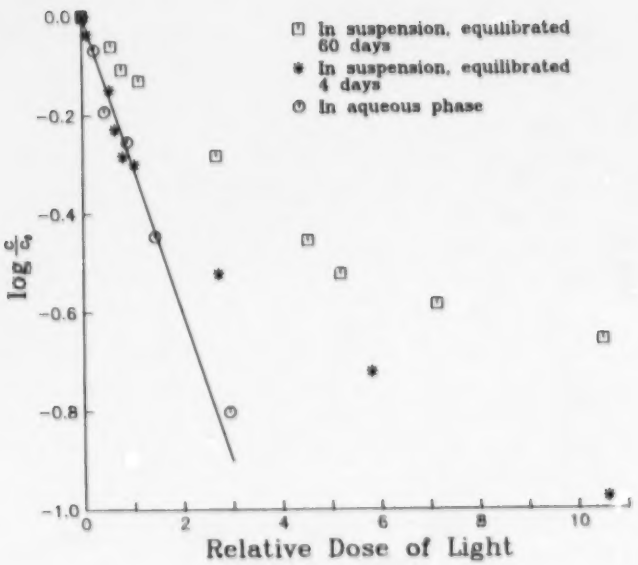


Figure 1. Photoreaction of DDE in EPA-12 sediment suspension (80 mg/liter) and in aqueous phase of the sediment suspension.

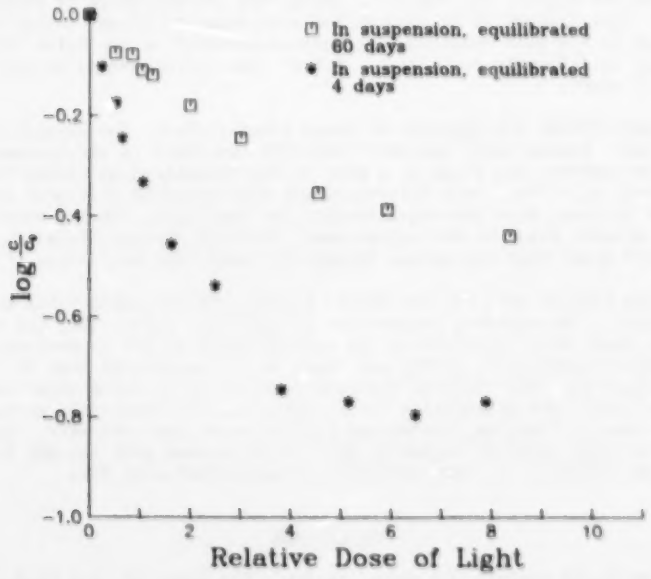


Figure 2. Photolysis of DDE in EPA-26 sediment suspension (100 mg/liter) equilibrated 4 days or 60 days.

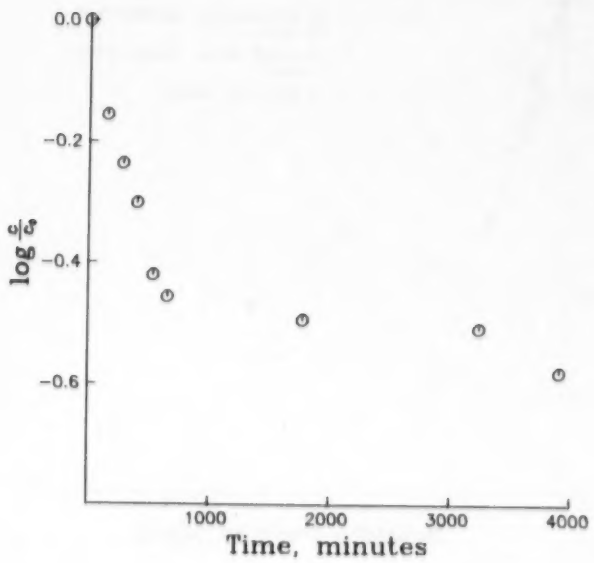


Figure 3. Photolysis of DDE in EPA-13 sediment suspension, after equilibration for 4 weeks.

sorbed to the suspended sediments in all systems. Data in Figures 1 and 2 were obtained using the same equipment and procedures. Less detailed studies of EPA-13 sediments were conducted in a different reaction vessel. In Figures 1 and 2, the concentration is plotted versus the "relative dose of light," which is defined as the dose received (light intensity times irradiation time) divided by the dose required to transform one-half of the total DDE in the EPA-12 suspension that was equilibrated for 4 days. Actual time corresponding to one dose unit ranged from 13 hours to 17 hours.

Several distinct effects are observed in these kinetic runs. The kinetic data deviate from first order behavior. Beyond about two halflives (75% reaction) in the systems that were equilibrated for two months, the slope of a plot of log concentration versus time was smaller than during the first halflife. This flattening was also observed at higher conversions in the DDE-suspension mixtures that were equilibrated for four days. On the other hand, photolysis of DDE in the aqueous phase of the suspensions, isolated by centrifugation, could be described by a first order rate expression through at least four half-lives (Figure 1).

In contrast, the kinetic data for the phenyl ketone, MTB (2), were first order with respect to MTB concentration in the sediment suspensions (Figure 4). Unlike DDE, the more hydrophilic MTB was completely (over 95%) dissolved in the aqueous phase of the suspensions. The first order rate constant for photolysis of MTB was lower in the suspension than in the filtrate of the suspension (Figure 4). The ratio of the rate constants with and without sediments present is assumed to equal the light attenuation factor, that is, the fractional decrease in average light intensity caused by light absorption and scattering by the sediments. Because MTB absorbs light in the same spectral region as DDE, it is assumed that the DDE in the suspension experienced the same decrease in light intensity as determined with MTB.

DISCUSSION

Several theories could explain the above results. The scope of this study was such that insufficient data could be obtained to adequately test the generality of any theory. Experiments and mathematical analyses of the data were conducted to test the predicted consequences of several hypotheses, however.

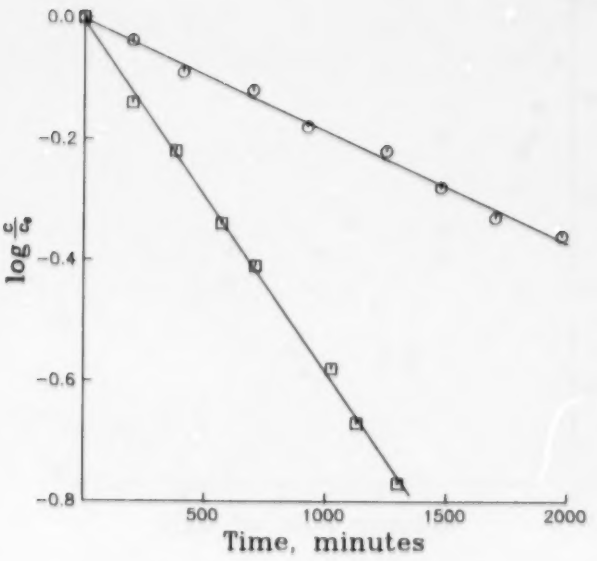
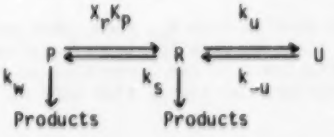


Figure 4. Comparison of photolysis of MTB in filtrate of EPA-12 suspension (plot A) and in the suspension of EPA-12 sediments (80 mg/liter, plot B).

One theory is that the experimental results could be attributable to changes in the properties of the suspended sediments. Such changes could possibly have resulted from thermal or biological degradation of natural photosensitizers on the sediment surface or by physical changes in the sediments resulting from stirring. The flattening observed in the kinetic plots with increasing dose of light might have been caused by photodegradation of sensitizers on the sediment surface. To test this idea, DDE was added to a suspension of EPA-12 sediments and the resulting mixture was equilibrated for 60 days. Then, the suspension was irradiated extensively (140 hours or 10 relative dose units of light) until the kinetic plot almost flattened (Fig. 1). At this point, the irradiation was stopped, DDE was re-added via sublimation, and the suspension was equilibrated for 4 days and then re-irradiated as before. The kinetic data were almost identical to those obtained using sediment that was not previously irradiated (Figure 5). These results, therefore, indicate that the photochemical properties of the EPA-12 sediment do not appear to change with exposure to ultraviolet irradiation or with prolonged equilibration time.

Another hypothesis, consistent with Karickhoff's interpretation of sorption kinetics (4), is that the sorbed DDE, although predominantly photoreactive within a short equilibration period, gradually diffuses into a microenvironment where the chemical is unreactive. The proposed kinetic model is shown below:



P represents the concentration of DDE dissolved in the aqueous phase of the suspension. The dissolved DDE is assumed to be in equilibrium with a fraction, X_r, of the sorbed DDE, which is present at concentration R and which is photoreactive. The remaining sorbed DDE, present at concentration U, is unreactive and is in equilibrium with the DDE sorbed in the reactive part. The partition coefficient K_p is the ratio of the total sorbed concentration to the dissolved concentration at equilibrium. The terms k_w and k_s are first order rate constants

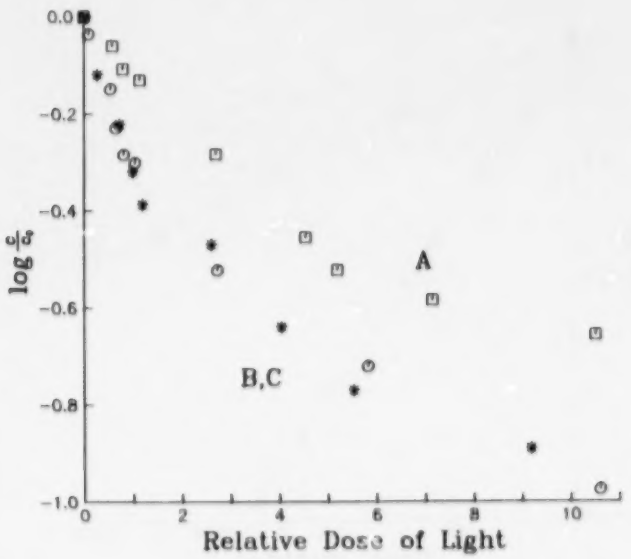


Figure 5. Comparison of photolysis kinetic data for DDE in EPA-12 sediment suspensions under various conditions: A, DDE equilibrated 2 months in suspension prior to photolysis; B, DDE readded to photolyzed suspension of plot A, then photolyzed again after equilibrating for 4 days; C, DDE equilibrated 4 days in EPA-12 suspension that was not irradiated.

for photolysis of DDE in the aqueous phase and reactive sorbed state, respectively; k_u and k_{-u} are first order rate constants for diffusion of the sorbed DDE into and back out of the unreactive microenvironment.

The following procedures and equations were employed to determine values for the various kinetic parameters that are listed in Table 2.

- k_w was assumed to equal the first order rate constant for photolysis of DDE dissolved in the filtrate of the sediment suspensions multiplied by the light attenuation factor. The latter was determined from the MTB results that are described above. The size of photolysis rate constants is proportional to light intensity, and so k_w and k_s were expressed in terms of relative dose units, DU^{-1}, to permit direct comparison from one run to another. Because less than 5% of the DDE in the suspensions was dissolved in most of these experiments, it can be readily demonstrated that photolysis in the aqueous phase makes a negligible contribution to the transformation of the reactive part of the DDE in the suspensions. Thus, a simpler kinetic model that ignores the aqueous phase was used to complete the kinetic analysis.

- If it is assumed that k_u is much smaller than k_s, then, when exposure time t is much larger than $1/k_s$, the rate limiting step for transformation approximately becomes equal to the rate of diffusion from the unreactive to the reactive microenvironment (eq. 1). Equation 1 describes the nearly flat part of the curves in Figures 1 to 3, where

$$\frac{C}{C_0} = \frac{U_0}{C_0} e^{-k_{-u}t} \qquad (1)$$

U_0 is the concentration in the unreactive state at the start of the photolysis and U_0/C_0 approximately equals $(1-X_r)$ in these systems. By least-squares linear regression on portions of the plots that exceeded four relative dose units, employing actual time on the abscissa and assuming the intercept equals $(1-X_r)$, k_{-u} and X_r were computed for each kinetic run.

- When exposure time is much shorter than $1/k_u$, then transformation is dominated by a decrease in R and the kinetic data are described by eq. 2 or its equivalent, eq. 3. In eq. 2 R_o is the concentration of reactive DDE at start of irradiation.

$$\frac{C}{C_o} = \frac{R_o e^{-k_s t} + U_o}{C_o} \qquad (2)$$

$$\frac{C}{C_o} - (1-X_r) = X_r e^{-k_s t} \qquad (3)$$

By employing X_r values from the preceding analysis, k_s values were computed using a least squares linear regression.

- Approximate values of $(k_u + k_{-u})$ were computed using eq. 4, a standard equation that describes kinetic data in equilibrium systems.

$$\frac{(X_r)_{96} - (X_r)_e}{1-(X_r)_e} = e^{-(k_u + k_{-u})t} \qquad (4)$$

$(X_r)_{96}$ and $(X_r)_e$ represent the fraction of reactive, sorbed DDE after four days and at equilibrium, respectively. For this computation, it was assumed that equilibrium was attained after equilibrating the DDE-sediment mixtures for two months.

Table 2. Kinetic parameters describing photoreaction of sorbed DDE in sediment suspensions.

Parameter	Sediment EPA-12	EPA-26	EPA-13
$(X_r)_e$	0.56	0.43	0.62
$(X_r)_{96\ hr}$	0.67	0.74	[a]
k_{-u}, hr^{-1}	5.8×10^{-3}	3.7×10^{-3}	4.7×10^{-3}
$(k_u + k_{-u})$, hr^{-1}	1.4×10^{-2}	6.3×10^{-3}	[a]
Light attenuation factor	0.33	0.30	[a]
k_w, DU^{-1}	0.23	0.20	[a]
4-day k_s, DU^{-1}	1.3	1.0	[a]
60-day k_s, DU^{-1}	0.74	0.64	[a]
4-day k_s/k_w	5.5	5.1	[a]
60-day k_s/k_w	3.2	3.1	[a]

[a] Not determined

Several interesting conclusions can be reached by examining the results of these calculations (Table 2).

(1) The calculations are self consistent. The rate constant $(k_u + k_{-u})$ is about a factor of two larger than k_{-u} although different approaches were used to compute both constants. Moreover, the factor of two is consistent with the theoretical prediction that diffusion should proceed at the same rate in all directions.

(2) The results are consistent with the previous findings of Karickhoff (4). The values of X_r at equilibrium lie between 0.4 and 0.6, the same range Karickhoff observed for the readily exchangeable portion of sorbed aromatic hydrocarbons. Moreover,

values of k_{-u} observed in the present study are very close to what would be predicted by Karickhoff's findings that desorption rate constants are inversely proportional to K_p. For example, K_p for DDE on EPA-26 was 14000, about 11 times greater than K_p for pyrene on the same sediment (4). The reciprocal relationship predicts a k_{-u} of 2.8×10^{-3} hr^{-1}, versus an observed value of 3.7×10^{-3} hr^{-1}.

(3) As previously determined by Miller and Zepp (2), the DDE sorbed in the reactive microenvironment is more photoreactive than when dissolved in water. The value of k_s changed less than a factor of two between equilibration times of 4 days and 2 months. Also, the value of k_s was very similar on both EPA-12 soil and EPA-26 sediment.

Although the above discussion points out strong similarities between these results and Karickhoff's studies (4), additional work revealed some inconsistencies. In the previous studies (4), Karickhoff found that the nonlabile part of the sorbed pollutants requires weeks for extraction by aprotic organic solvents, whereas the labile part was readily extractable. If the labile part corresponds to the reactive component observed in this study, then the ratio of isooctane-extractable to total extractable DDE should decrease with increasing dose of light. Although the isooctane did not extract more than 70% of the sorbed DDE, a statistically significant decrease in this ratio was not observed as photoreaction of DDE on the three sediments proceeded.

SUMMARY

The photoreaction of DDE on several natural sediments could be described by a kinetic model in which the DDE is sorbed in two types of microenvironments, one in which it is more photoreactive than when dissolved in water and another in which it is completely unreactive. Analysis of the kinetic data indicates that sorption on the unreactive part of the sediments occurs much more slowly than on the reactive part. At equilibrium, about half of the sorbed DDE was unreactive with the three sediments studied here. The kinetic results, although limited, are consistent with prior studies of sorption kinetics by Karickhoff.

ACKNOWLEDGEMENT

We acknowledge the technical assistance of Mr. Kenneth Morris and Mr. Merritt Sink and the helpful comments and analyses of the data received from Dr. Samuel Karickhoff and Mr. George L. Baughman.

REFERENCES

(1) Oliver, B. G., Cosgrove, E. G., Carey, J. H., Environ. Sci. Technol., 13, 1075 (1979).

(2) Miller, G. C., Zepp, R. G., Environ. Sci. Technol., 13, 860(1979).

(3) Miller, G. C., Zepp, R. G., Water Research, 13, 453(1979).

(4) Karickhoff, S. W., in "Contaminants and Sediments, Volume 2," R. A. Baker, Ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1980, pp 193-205.

(5) Zepp, R. G., Wolfe, N. L., Azarraga, L. V., Cox, R. H., Pape, C., Arch. Environ. Contam. Toxicol., 6, 305(1977).

(6) Means, J. C., Wood, S. G., Hassett, J. J., Banwart, W. L., Environ. Sci. Technol., 14, 1524(1980).

(7) Holm, H. W., Cox, M. F., Appl. Microbiol., 27, 622(1974).

(8) Hatchard C. G., Parker, C. A., Proc. Roy. Soc. (London), A235, 518(1956).

Note: Mention of company names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

(Received in USA 2 April 1981)